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Ammonia Borane Dehydrogenation Catalyzed by (κ^4-EP3)Co(H) [EP3= E(CH2CH2PPh2)3; E = N, P] and H2Evolution from Their Interaction with NH Acids

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Abstract

© 2017 American Chemical Society. Two Co(I) hydrides containing the tripodal polyphosphine ligand EP 3 , (κ 4 -EP 3)Co(H) [E(CH 2 CH 2 PPh 2) 3 ; E = N (1), P (2)], have been exploited as ammonia borane (NH 3 BH 3 , AB) dehydrogenation catalysts in THF solution at T = 55 °C. The reaction has been analyzed experimentally through multinuclear (11 B, 31 P{ 1 H}, 1 H) NMR and IR spectroscopy, kinetic rate measurements, and kinetic isotope effect (KIE) determination with deuterated AB isotopologues. Both complexes are active in AB dehydrogenation, albeit with different rates and efficiency. While 1 releases 2 equiv of H 2 per equivalent of AB in ca. 48 h, with concomitant borazine formation as the final "spent fuel", 2 produces 1 equiv of H 2 only per equivalent of AB in the same reaction time, along with long-chain poly(aminoboranes) as insoluble byproducts. A DFT modeling of the first AB dehydrogenation step has been performed, at the M06//6-311++G∗ level of theory. The combination of the kinetic and computational data reveals that a simultaneous B-H/N-H activation occurs in the presence of 1, after a preliminary AB coordination to the metal center. In 2, no substrate coordination takes place, and the process is better defined as a sequential BH 3 /NH 3 insertion process on the initially formed [Co]-NH 2 BH 3 amidoborane complex. Finally, the reaction of 1 and 2 with NH-acids [AB and Me 2 NHBH 3 (DMAB)] has been followed via VT-FTIR spectroscopy (in the -80 to +50 °C temperature range), with the aim of gaining a deeper experimental understanding of the dihydrogen bonding interactions that are at the origin of the observed H 2 evolution.

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